Hydrogenation and Dehydrogenation Behavior of $\text{LaNi}_{5-x}\text{Co}_x$ ($x = 0, 0.25, 2$) Alloys Studied by Pressure Differential Scanning Calorimetry

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The hydrogenation and dehydrogenation behavior of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 was studied by the pressure differential scanning calorimetry (PDSC) at the hydrogen pressure range of 1 to 5 MPa in the temperature range from 323 to 473 K with the heating and cooling rates of 2 to 30 K min⁻¹. In the heating run of the hydride of LaNi_5 , two endothermic peaks were observed. One was the peak for the transformation from the γ phase (full hydride LaNi_5H_6) to the β phase (hydride LaNi_5H_3). The other was the peak for the transformation from the β phase to the α phase (solid solution). In the cooling run, one exothermic peak for the transformation from the α phase to the γ phase was observed. These endothermic and exothermic peaks shifted to higher temperatures with the increase in hydrogen pressure. In the heating and cooling runs of the $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ system the PDSC curves similar to those of the $\text{LaNi}_5\text{-H}_2$ system were observed. However, in the heating run of the hydride of LaNi_3Co_2 only one endothermic peak was observed. Using Ozawa's method, the activation energies for dehydrogenation of the hydrides were estimated. The activation energy for the γ - β transformation was higher than that for the β - α transformation. Substitution of cobalt for a part of nickel in LaNi_5 increased the activation energies for the phase transformations.

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1. Introduction

The intermetallic compound LaNi_5 is a well-known hydrogen storage alloy. Many physical and chemical properties of the hydride of LaNi_5 such as hydrogen storage capacity, operation temperature, crystal structure, occupation site of hydrogen, etc. have been studied by many research groups.¹⁾ On the pressure-composition isotherms of the $\text{LaNi}_5\text{-H}_2$ system, Ono *et al.*²⁻⁴⁾ have observed that the β phase (hydride LaNi_5H_3) is formed between the α phase (solid solution) and the γ phase (full hydride LaNi_5H_6) in the desorption process above 343 K and in the absorption process above 367 K. Furthermore, *in-situ* X-ray and neutron diffraction measurements⁵⁻⁸⁾ have shown that the space group of the α and β phases is $P6/mmm$ and that of the γ phase is $P6_3mc$. However, little is known about the kinetics of the transformation between these phases in the processes of hydrogenation and dehydrogenation. To study the phase transformation of the hydrides, the pressure differential scanning calorimetry (PDSC) is suitable, because the phase transformations can be easily found out by their endothermic and exothermic reactions in the calorimetry. Furthermore, the activation energy for the phase transformation can be determined by Ozawa's method⁹⁾ in the measurements of DSC with different heating and cooling rates.

It has been recognized that the substitution of cobalt for a part of nickel in LaNi_5 is effective in descent of plateau pressure¹⁰⁾ and in extension of life time for the hydrogen storage materials.¹¹⁾ With the substitution of cobalt for nickel in LaNi_5 the lattice constant increases,¹⁰⁾ while the dislocation density¹²⁾ and the vacancy concentration¹³⁾ induced by hydrogenation decreases. However, effect of cobalt substitution on the kinetics of hydrogenation and dehydrogenation of LaNi_5 has not been studied, so far.

The present work has been performed to reveal the hydrogenation and dehydrogenation kinetics of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 by PDSC at the hydrogen pressure range of 1 to 5 MPa in the temperature range from 323 to 473 K with the heating and cooling rates of 2 to 30 K min⁻¹.

2. Experimental

2.1 Sample preparation and characterization

Buttons of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 alloys were prepared by arc melting pellets of pure metals (La: 99.9 mass%, Ni: 99.95 mass%, Co: 99.9 mass%) in an argon atmosphere. The buttons were annealed at 1223 K for 48 h in an argon atmosphere for homogenization. Chemical analysis by SEM-EDX showed that the alloys were in the nominal compositions. Furthermore, X-ray diffraction with $\text{CuK}\alpha$ radiation showed that the crystal structure of the alloys was of the CaCu_5 -type. Then, the buttons were crushed into small particles with the mean diameter of 1 mm or less.

2.2 Measurement of PDSC curve

The crushed particles (masses from 10 to 60 mg) of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 were set in the PDSC apparatus (Mac Science, model: 3520S), and hydriding and dehydriding processes were repeated 10 times at the hydrogen pressure of 5 MPa in the temperature range from 323 to 473 K (323 to 573 K for LaNi_3Co_2 , because the temperature of hydriding-dehydriding is above 473 K) with the heating and cooling rate of 30 K min⁻¹.

The PDSC curves for the hydriding and dehydriding processes of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 alloys were measured at the hydrogen pressure of 1 to 5 MPa in the temperature range from 323 to 473 K (323 to 573 K for LaNi_3Co_2) with the heating and cooling rates of 2 to 30 K min⁻¹. Hydrogen gas of 7 N purity was used.

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2.3 Ozawa's method

By the analysis of the PDSC curve, the activation energy E for the phase transformation of the hydrides was determined. On the assumption that the reaction rate of a single process is measured with a constant heating or cooling rate ϕ , the relationship between ϕ and E is expressed as follows:⁹⁾

$$\log \phi + 0.4567E/RT_p = \text{const.} \quad (1)$$

where T_p is the temperature of the peak top. The plot of $\log \phi$ against the reciprocal of T_p shows a straight region, and the slope gives the value of $-0.4567E/R$.

3. Results and Discussion

3.1 PDSC curves of hydrides of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2

Figure 1 shows the PDSC curves of the $\text{LaNi}_5\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} at the hydrogen pressure range of 1 to 5 MPa. In the heating runs, dehydrogenation processes occur, where two endothermic peaks are observed at each heating run. With the increase in hydrogen pressure, both peaks shift to higher temperatures and the height of the first peak at lower temperature decreases and becomes broad in the lower temperature side. The appearance of the two peaks during the heating run of the $\text{LaNi}_5\text{-H}_2$ system in the PDSC^{14,15)} and the DTA¹⁶⁾ has been already found. Akiba *et al.*⁴⁾ have measured the pressure-composition (P-C) isotherm of the $\text{LaNi}_5\text{-H}_2$ system and observed a gap in the plateau of the desorption process above 343 K. In combination with *in-situ* X-ray diffraction measurements, they have deduced that the gap in the plateau corresponds to the formation of the β phase. At the temperature of 413 K, the gap appears with the hydrogen pressure of 5 MPa.⁴⁾ Hence, we confirmed the $\gamma\text{-}\beta$ transformation of the $\text{LaNi}_5\text{-H}_2$ system at the hydrogen pressure of 5 MPa by the PDSC, as shown in Fig. 2. On the heating run at the rate of 2 K min^{-1} up to 413 K, one endothermic peak was observed. After holding at 413 K for 5 min, the cooling run at the rate of 2 K min^{-1} started down to 343 K. During the cooling run, one exothermic peak was observed. After holding 343 K for 5 min, the heating run was repeated and again two endothermic peaks were observed. Therefore, the formation of the β phase in

the $\text{LaNi}_5\text{-H}_2$ system at 413 K with the hydrogen pressure of 5 MPa was confirmed, as observed by Akiba *et al.*⁴⁾ Thus, the first peak at lower temperature in the dehydrogenation process shown in Fig. 1 corresponds to the $\gamma\text{-}\beta$ transformation and the second peak at higher temperature corresponds to the $\beta\text{-}\alpha$ transformation. On the other hand, the height of the second peak is nearly independent of hydrogen pressure. The difference in the temperatures of the two peaks increases with the increase in hydrogen pressure.

In the cooling runs, the hydrogenation process occurs. As shown in Fig. 1, at each cooling run with the cooling rate of 2 K min^{-1} a single exothermic peak is observed apparently. With the increase in hydrogen pressure, the peak shifts to higher temperatures and the height of the peak decreases, although a broad weak peak appears at lower temperatures. To elucidate the problem why only one peak is observed in the hydrogenation process, the PDSC curves of the $\text{LaNi}_5\text{-H}_2$ system at the hydrogen pressure of 5 MPa were examined with the slow rate of 1 K min^{-1} for heating and cooling runs, as shown in Fig. 3. Even in the cooling run as well as the heating run, two peaks are observed, that is, in the hydrogenation process, the first peak at higher temperature corresponds to

Fig. 1 PDSC curves of the $\text{LaNi}_5\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} .

Fig. 2 PDSC curve of the $\text{LaNi}_5\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} at the hydrogen pressure of 5 MPa.

Fig. 3 PDSC curves of the $\text{LaNi}_5\text{-H}_2$ system with the heating and cooling rate of 1 K min^{-1} at the hydrogen pressure of 5 MPa.

Fig. 4 PDSC curves of the $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} .

Fig. 5 PDSC curves of the $\text{LaNi}_3\text{Co}_2\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} .

the α - β transformation and the second peak at lower temperature to the β - γ transformation. However, in the cooling run of 2 K min^{-1} with the hydrogen pressure of 5 MPa, the separation of the peaks is not clear, but it seems that the peak is composed with three peaks. The main peak is due to the transformation from the α phase to the β phase. A small peak and a broad weak peak at lower temperatures are due to the transformation from the β phase to the γ phase. However, these peaks come close together at lower hydrogen pressure. Finally, at 1 MPa the peaks become single one. This behavior has been also recognized in the P-C isotherms of the $\text{LaNi}_5\text{-H}_2$ system.⁴⁾ In the plateau a gap which corresponds to the formation of the β phase is observed at higher pressure of hydrogen, while the gap cannot be detected at lower pressure of hydrogen.

The PDSC curves of the $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} at the hydrogen pressure range of 1 to 5 MPa are shown in Fig. 4. In the heating runs, two endothermic peaks are observed. Both peaks shift to higher temperatures with the increase in hydrogen pressure, as in the case of the PDSC for the $\text{LaNi}_5\text{-H}_2$ system. However, the first peak which corresponds to the γ - β transformation is weak in comparison with that of the $\text{LaNi}_5\text{-H}_2$ system shown in Fig. 1. In the PDSC curve, the intensity of a peak represents the enthalpy change for the transformation. Therefore, it seems that the substitution of cobalt for a part of nickel in LaNi_5 restricts the formation of the γ hydride phase. With the increase in hydrogen pressure, the first peak decreases and spreads over a wide temperature range. In the cooling runs, a single exothermic peak is observed. With the increase in hydrogen pressure, the peak shifts to higher temperatures, while the height of the peak is nearly independent of hydrogen pressure. However, with the increase in hydrogen pressure a broad weak peak appears at lower temperature. This is probably due to the increase in the difference in the temperatures for the α - β and the β - γ phase transformations at high pressures, as in the cooling runs of the $\text{LaNi}_5\text{-H}_2$ system in Fig. 1.

Figure 5 shows the PDSC curves of the $\text{LaNi}_3\text{Co}_2\text{-H}_2$ system with the heating and cooling rate of 2 K min^{-1} at the hydrogen pressure range of 1 to 5 MPa. In contrast to the heating runs of the hydrides of LaNi_5 and $\text{LaNi}_{4.75}\text{Co}_{0.25}$, a single endothermic peak appears in the dehydrogenation process of

Fig. 6 P-C isotherms of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 in the fifth cycle of desorption at 313 K.

the $\text{LaNi}_3\text{Co}_2\text{-H}_2$ system. This means that the γ phase is seldom formed by the substitution of cobalt up to the compound LaNi_3Co_2 . The height of the peak decreases with the increase in hydrogen pressure. In the cooling runs, a single exothermic peak is observed, which corresponds to the formation of the β phase. No satellite peak appears. To elucidate the effect of cobalt substitution on the plateau region in the P-C isotherm, the P-C isotherms at 313 K (the desorption process of the fifth cycle) of $\text{LaNi}_5\text{-H}_2$, $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ and $\text{LaNi}_3\text{Co}_2\text{-H}_2$ systems were measured, as shown in Fig. 6. With the increase in the substitution quantity of cobalt, the plateau region becomes short. The substitution of cobalt makes the plateau region short because the formation of the γ phase is restricted.

3.2 Activation energies for the transformations of the hydride phases

Figures 7(a), (b) and (c) shows the PDSC curves of the $\text{LaNi}_5\text{-H}_2$, $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ and $\text{LaNi}_3\text{Co}_2\text{-H}_2$ systems at the hydrogen pressure of 5 MPa with the heating and cooling rates of 2 to 30 K min^{-1} , respectively. With the increase in the heating rate, the height of the endothermic peaks increases remarkably and the peak temperatures shift slightly to higher temperatures, whereas with the increase in the cooling rate the height of the exothermic peak increases remarkably and the peak temperature shifts slightly to lower temperatures. All of the $\text{LaNi}_5\text{-H}_2$, $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ and $\text{LaNi}_3\text{Co}_2\text{-H}_2$ systems show similar tendency in the PDSC curves at the hydrogen pressure of 1 to 5 MPa with the heating and cooling

rates of 2 to 30 K min^{-1} . From the shift of the peak temperature, Ozawa's plots of dehydrogenation processes of the $\text{LaNi}_5\text{-H}_2$, $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ and $\text{LaNi}_3\text{Co}_2\text{-H}_2$ systems are obtained, as shown in Figs. 8(a), (b) and (c), respectively. Using eq. (1) and the linear slope in Figs. 8(a), (b) and (c), the activation energies for dehydrogenation processes of the hy-

Fig. 7 PDSC curves of (a) $\text{LaNi}_5\text{-H}_2$, (b) $\text{LaNi}_{4.75}\text{Co}_{0.25}\text{-H}_2$ and (c) $\text{LaNi}_3\text{Co}_2\text{-H}_2$ systems at the hydrogen pressure of 5 MPa with the heating and cooling rates of 2 to 30 K min^{-1} .

Fig. 8 Ozawa's plots for dehydrogenation of hydrides of (a) LaNi_5 , (b) $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and (c) LaNi_3Co_2 .

Fig. 9 Activation energy for dehydrogenation of hydrides of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 at the hydrogen pressure of 1, 3 and 5 MPa.

hydrides of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 are estimated. Figure 9 shows the hydrogen pressure dependence of the activation energies for the phase transformations of the hydrides. All the activation energies increase with the increase in hydrogen pressure. For the hydrides of LaNi_5 and $\text{LaNi}_{4.75}\text{Co}_{0.25}$, the activation energy for the γ - β transformation is higher than that for the β - α transformation. The substitution of cobalt for a part of nickel in LaNi_5 made the activation energies for both of the γ - β and the β - α transformations high. This means that the substitution of cobalt increases the thermodynamic stability of the β and γ phases. This difference in the stabilities of the hydrides can be also explained by the descent of the plateau pressure with increase of the quantity substituted by cobalt, as shown in Fig. 6.

4. Conclusions

The hydrogenation and dehydrogenation behavior of LaNi_5 , $\text{LaNi}_{4.75}\text{Co}_{0.25}$ and LaNi_3Co_2 was studied by the pressure differential scanning calorimetry at the hydrogen pres-

sure range of 1 to 5 MPa in the temperature range from 323 to 473 K (323 to 573 K for LaNi_3Co_2) with the heating and cooling rates of 2 to 30 K min⁻¹. Using Ozawa's method, the activation energies for dehydrogenation of the hydrides were estimated. The activation energies for the phase transformations of dehydrogenation increase with the increase in hydrogen pressure. The activation energy for the γ - β transformation is higher than that for the β - α transformation, and the substitution of cobalt for a part of nickel in LaNi_5 increases the activation energies for the phase transformations.

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